533 Rec'd PCT/PTO 15 AUG 2001

U.S. DEPARTMENT OF COMMERCE PATENT & TRADEMARK OFFICE

B/O Form PTO-1390 **Transmittal Letter to the United States Designated/Elected Office (DO/EO/US) Concerning a Filing Under *35 USC 371***		*Attorney's Docket Number* PICK3001/REF *U.S. Application Number (if known)* 09/926018
International Application Number PCT/GB00/00513	*International Filing Date* 15 February 2000	*Priority Date Claimed* 16 February 1999
Title of Invention PRECIPITATION PROCESS		
Applicant(s) for DO/EO/US PICKERING et al.		

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items under *35 USC 371*:

1. ☒ This is a **FIRST** submission of items concerning a filing under *35 USC 371*.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under *35 USC 371*.
3. ☒ This express request to begin national examination procedures *(35 USC 371(f))* at any time rather than delay examination until the expiration of the applicable time limit set in *35 USC 371(b)* and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed *35 USC 371(c)(2)*.
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English *(35 USC 371(c)(2))*.
7. ☒ Amendments to the claims of the International Application under PCT Article 19 *(35 USC 371(c)(3))*
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 *(35 USC 371(c)(3))*.
9. ☐ An oath or declaration of the inventor(s) *(35 USC 371(c)(4))*. (☐ Executed ☐ Unexecuted)
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 *(35 USC 371(c)(5))*.

Items 11 to 16 below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under *37 CFR 1.97* and *1.98*.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with *37 CFR 3.28* and *3.31* is included.
13. ☒ A **FIRST** preliminary amendment.
    ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: Applicants assert small entity status.

533 Rec'd PCT/PTO 15 AUG 2001

Application Number (if Known) 09/926018	*International Application Number* PCT/GB00/00513	*Attorney's Docket Number* PICK3001/REF	
		Calculations	**PTO USE ONLY**

17. The following fees are submitted: **Basic National Fee** ***(37 CFR 1.492(a)(1)-(5))*:** ☒ Search report has been prepared by the EPO or JPO . . . . $860.00 ☐ International Preliminary Examination Fee paid to USPTO *(37 CFR 1.482)* . . . . . $690.00 ☐ No International Preliminary Examination Fee paid to USPTO *(37 CFR 1.482)* but International Search Fee paid to USPTO *(37 CFR 1.445(a)(2))* . . . . $710.00 ☐ Neither International Preliminary Examination Fee *(37 CFR 1.482)* nor International Search Fee *(37 CFR 1.445(a)(2))* paid to USPTO . . . . $1000.00 ☐ International Preliminary Examination Fee paid to USPTO *(37 CFR 1.482)* and all claims satisfied provisions of PCT Article 33(1)-(4) $100.00				$860.00	
ENTER APPROPRIATE BASIC FEE AMOUNT				$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date *(37 CFR 1.492(e))*.					
CLAIMS	**NUMBER FILED**	**NUMBER EXTRA**	**RATE**		
Total Claims	27 -20 =	7	× $18.00	$ 126.00	
Independent Claims	1 -3 =	0	× $80.00	$ 0.00	
Multiple Dependent Claims (if applicable)			+ $270.00		
TOTAL OF ABOVE CALCULATIONS				$ 986.00	
Reduction by ½ for filing by small entity, if applicable. Small Entity Status is asserted pursuant to 37 CFR 1.27 for this application.				$ 493.00	
SUBTOTAL				$ 493.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date *(37 CFR 1.492(f))*.					
TOTAL NATIONAL FEE					
Fee for recording the enclosed assignment *(37 CFR 1.21(h))*. The assignment must be accompanied by an appropriate cover sheet *(37 CFR 3.28, 3.31)*. **$40.00** per property.					
TOTAL FEES ENCLOSED				$ 493.00	
			Amount to be:	Refunded:	
				Charged:	

a. ☒ A check in the amount of $493.00 to cover the fees is enclosed.
b. ☐ Please charge my **Deposit Account Number 02-0200** in the amount of $ ____________ to cover the above fees. A duplicate copy of this sheet is enclosed.
c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to **Deposit Account Number 02-0200**. A duplicate copy of this sheet is enclosed.

Note: Where an appropriate time limit under *37 CFR 1.494* or *1.495* has not been met, a petition to revive *(37 CFR 1.137(a) or (b))* must be filed and granted to restore the application to pending status.

BACON & THOMAS, PLLC
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ALEXANDRIA, VIRGINIA 223124-1176
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DATE: August 15, 2001

Respectfully submitted,

Richard E Fichter

Richard E. Fichter
Attorney for Applicant
Registration Number: 26,382

533 Rec'd PCT/PTO 15 AUG 2001
09/926018

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

PICKERING et al.

U.S. National Phase of PCT/GB00/00513

Entry papers filed herewith August 15, 2001

For: PRECIPITATION PROCESS

Attention: PCT OFFICE

PRELIMINARY AMENDMENT
AND INFORMATION DISCLOSURE STATEMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

The present application is the U.S. national phase of international application number PCT/GB00/00513. The following amendments pertain to the claims as amended.

Please note that the amended pages 26-30 attached to the International Preliminary Examination Report (Annexes) and submitted herewith, have replaced the originally filed pages 26-30 of the application. The claims to be examined and amended by this preliminary amendment are found on amended pages 26-30.

Please amend the above-identified application as follows:

IN THE SPECIFICATION:

Please add the attached ABSTRACT OF THE DISCLOSURE to the application.

IN THE CLAIMS:

Please replace claims 4-10, 12-13, 15, 17, and 19-27 with the following amended claims.

4(Amended). A process as claimed in claim 1, wherein the metal oxide which precipitates out of solution is a product of hydrolysis of the metal in its higher cationic oxidation state.

5(Amended). A process as claimed in claim 1, wherein the oxidant is added as an aqueous solution.

6(Amended). A process as claimed in claim 1, wherein the metal is selected from Ce or Fe.

7(Amended). A process as claimed in claim 1, wherein the aqueous solution of said metal in a lower cationic oxidation state comprises nitrate as a counter-ion.

8(Amended). A process as claimed in claim 1, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/1.

9(Amended). A process as claimed in claim 1, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/1.

10(Amended). A process as claimed in claim 1, wherein the oxidant comprises hydrogen peroxide.

12(Amended). A process as claimed in claim 10, wherein the metal in its lower oxidation state is Ce^{3+}, the metal in its higher oxidation state is Ce^{4+} and the metal oxide which precipitates has the general formula $Ce(OH)_{4-y}OOH_y$ wherein $y \geq 1$.

13(Amended). A process as claimed in claim 1, comprising the additional step of adding hydroxide ions to the reaction mixture so as to substantially complete the precipitation process.

15(Amended). A process as claimed in claim 1, comprising the further step of isolating the precipitate.

17(Amended). A process for the precipitation of a weakly agglomerated nanocrystalline powder of a metal oxide, which process comprises the steps of:

(i) inducing homogeneous precipitation of said metal oxide by a process according to claim 13; and

(ii) isolating the precipitate.

19(Amended). A process as claimed in claim 17 comprising the further step of washing and drying the precipitate.

20(Amended). A process as claimed in claim 17, wherein said hydrothermal treatment is at a temperature of from 100 to 300°C.

21(Amended). A process as claimed in claim 17, wherein said hydrothermal treatment is at a temperature of approximately 180°C.

22(Amended). A metal oxide obtained by a process as claimed in claim 1.

23(Amended). A weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as claimed in claim 17.

24(Amended). A metal oxide or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 23 having a mean particle size in the range of from

2 to 10 nm with a geometric standard deviation in the particle size less than or equal to 1.2.

25(Amended). A metal oxide or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 24 having a mean particle size in the range of from 2 to 5 nm with a geometric standard deviation in the particle size less than or equal to 1.1.

26(Amended). A metal oxide or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 24 which comprises cerium oxide.

27(Amended). A glass, a polishing medium for glass, a thin surface film, a phosphor, an oxygen storage material or catalyst material which has been manufactured by a process which uses a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 23.

REMARKS

Applicants have amended the claims in order to reduce the initial filing fee by deleting the multiple dependent claims from the application. Applicants retain the right to reintroduce any subject matter canceled by the present Amendment at any time during the prosecution of this application or any further application claiming benefit of this application.

Applicants have amended the application to substitute the originally filed pages 26-30 with the amended pages 26-30 attached to the International Preliminary Examiner Report (Annexes) and included in the application as filed herewith. Also, an Abstract of the Disclosure has been added to the application.

Applicants are submitting herewith a copy of the Search Report which issued on International Application No. PCT/GB00/00513, of which the present application is the U.S. national phase. All of the publications cited in the International Search Report are listed on the attached Form PTO-1449. It is Applicants' understanding that, under the procedures of the PCT, copies of the cited publications will have been supplied to the U.S. Patent Office by the International Bureau. However, the Examiner is invited to contact the undersigned attorney if additional copies are necessary or would facilitate examination of the present application.

Otherwise, the Examiner is respectfully requested to return an initialed and dated copy of the attached Form PTO-1449 to confirm that all publications listed thereon have been considered and made officially of record in the file of this application.

Applicants understand that, under the procedures of the PCT, a copy of the priority document (GB 9903519.8, filed 16 February 1999) will have been supplied to the U.S. Patent Office pursuant to Rule 17 of the PCT Regulations. It is therefore respectfully requested that the first Official Action in the present application contain an indication that the appropriate priority document is in the file of this application.

In view of the above amendments, an early action on the application is now in order and is most respectfully requested.

Respectfully submitted,
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DATE: August 15, 2001

Marked-Up Version Showing Changes Made

IN THE CLAIMS:

Please replace claims 4-10, 12-13, 15, 17, and 19-27 with the following amended claims.

4(Amended). A process as claimed in [any one of the preceding claims] claim 1, wherein the metal oxide which precipitates out of solution is a product of hydrolysis of the metal in its higher cationic oxidation state.

5(Amended). A process as claimed in [any one of the preceding claims] claim 1, wherein the oxidant is added as an aqueous solution.

6(Amended). A process as claimed in [any one of the preceding claims] claim 1, wherein the metal is selected from Ce or Fe.

7(Amended). A process as claimed in [any one of the preceding claims] claim 1, wherein the aqueous solution of said metal in a lower cationic oxidation state comprises nitrate as a counter-ion.

8(Amended). A process as claimed in [any one of the preceding claims] claim 1, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/1.

9(Amended). A process as claimed in [any one of the preceding claims] claim 1, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/1.

10(Amended). A process as claimed in [any one of the preceding claims] claim 1, wherein the oxidant comprises hydrogen peroxide.

12(Amended). A process as claimed in claim 10 [or claim 11], wherein the metal in its lower oxidation state is Ce^{3+}, the metal in its higher oxidation state is Ce^{4+} and the metal oxide which precipitates has the general formula $Ce(OH)_{4-y}OOH_y$ wherein $y \geq 1$.

13(Amended). A process as claimed in [any one of the preceding claims] claim 1, comprising the additional step of adding hydroxide ions to the reaction mixture so as to substantially complete the precipitation process.

15(Amended). A process as claimed in [any one of the preceding claims] claim 1, comprising the further step of isolating the precipitate.

17(Amended). A process for the precipitation of a weakly agglomerated nanocrystalline powder of a metal oxide, which process comprises the steps of:

(i) inducing homogeneous precipitation of said metal oxide by a process according to claim 13 [or claim 14]; and

(ii) isolating the precipitate.

19(Amended). A process as claimed in claim 17 [or claim 18] comprising the further step of washing and drying the precipitate.

20(Amended). A process as claimed in [any one of claims 17 to 19] claim 17, wherein said hydrothermal treatment is at a temperature of from 100 to 300°C.

21(Amended). A process as claimed in [any one of claims 17 to 20] claim 17, wherein said hydrothermal treatment is at a temperature of approximately 180°C.

22(Amended). A metal oxide obtained by a process as claimed in [any one of claims 1 to 16] claim 1.

23(Amended). A weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as claimed in [any one of claims 17 to 21] claim 17.

24(Amended). A metal oxide [as claimed in claims 22] or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 23 having a mean particle size in the range of from 2 to 10 nm with a geometric standard deviation in the particle size less than or equal to 1.2.

25(Amended). A metal oxide [as claimed in claim 22 or claim 24] or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim [23 or claim] 24 having a mean particle size in the range of from 2 to 5 nm with a geometric standard deviation in the particle size less than or equal to 1.1.

26(Amended). A metal oxide [as claimed in any one of claims 22, 24 or 26] or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in [any one of claims 23, 24 or 25] claim 24 which comprises cerium oxide.

27(Amended). A glass, a polishing medium for glass, a thin surface film, a phosphor, an oxygen storage material or catalyst material which has been manufactured by a process which uses a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in [any one of claims 23, 24, 25 or 26] claim 23.

ABSTRACT OF THE DISCLOSURE

The present invention relates to a process for inducing homogeneous precipitation of a metal oxide, wherein said metal is capable of existing in at least two cationic oxidation states, which process comprises the steps of: i) providing an aqueous solution of a metal in a lower cationic oxidation state; and ii) adding an oxidant capable of oxidising said metal to a higher cationic oxidation state under conditions such that the mixing of said aqueous solution and said oxidant is substantially complete before precipitation of an oxide of said metal in its higher oxidation state occurs.

Precipitation Process

The present invention is concerned with a process for inducing homogeneous precipitation of metal oxides and with the application of such a process to the preparation of weakly agglomerated nanocrystalline powders of said metal oxides.

In the present specification the term "metal oxides" is intended to include hydroxides, hydrated oxides, oxohydroxides, or oxoperoxohydroxides of metals.

The increased mechanical performance demanded of advanced ceramic materials imposes increasingly stricter requirements on the ceramic powders from which they are made. The use of monodisperse nanocrystalline powders as starting materials has demonstrated considerable potential for improving the functional properties of existing ceramic compositions. For example, the use of monodisperse nanocrystalline powders as starting materials provides ceramic compositions with finer porosity (e.g. for use in ceramic filters), and greater surface area (e.g. for use in catalysts). Such materials are also capable of forming better thin ceramic coatings.

In the present specification the term "nanocrystalline powder" is intended to mean a powder wherein substantially all of the constituent particles have a crystal size of less than 100nm.

The term "weakly agglomerated powder" is intended to mean a powder containing agglomerates that break up during normal processing or forming operations.

The term "monodisperse powder" is intended to mean a powder whose particle size distribution has a geometric standard deviation, σ_g, less than or equal to 1.1. For many conventional powders σ_g would be in the range of from 1.8 to 2.2.

Cerium (IV) oxide, CeO_2, is an example of a material where the number of applications has increased rapidly, for example in glasses, phosphors, catalysis, and chemical applications, and for which the use of nanocrystalline powders is an important factor. Unfortunately, the high specific surface areas of nanocrystalline powders, in which the primary particle size is often smaller than 5nm, also results in a stronger tendency of the powder to agglomerate which can make processing difficult. In the present specification the term "primary particle" distinguishes the small individual particles (typically less than 5nm in diameter) that are formed in the first stage of the homogeneous precipitation process from the larger agglomerates of such particles (typically 50-100nm in diameter) that may form later. These large spherical agglomerates are referred to as "secondary particles" and may contain hundreds of primary particles. Weakly-agglomerated powder is needed both for dry processing methods, for example powder compaction, and for the preparation of stable suspensions in liquids, for example for thin or thick film production. Unless weakly-agglomerated nanoscale powders can be produced, the benefits expected from highly-uniform nanocrystalline powders are easily lost during the manufacture of components. The strength of agglomerates depends on the surface properties of the nanocrystalline particles in the powder and these properties are sensitively dependent on the powder

synthesis procedures.

Precipitation from aqueous metal salt solution is widely used in industry for producing ceramic oxide powders, but for nanocrystalline materials, such powders tend to form excessively hard agglomerates. The precipitated species is usually a precursor, for example a hydroxide, rather than the required oxide and a thermal decomposition treatment is needed to obtain the final product. In densely agglomerated nanostructured powders there are many points of contact between primary particles and even a low-temperature thermal decomposition treatment allows sufficient diffusion to occur to produce agglomerates too hard to be easily redispersed. Dense agglomerates must therefore be avoided during the precipitation process if easily processable powders are to be obtained. Control of agglomerate morphology requires control of the chemistry of the precipitation reaction.

Precipitation occurs by adding a precipitating ligand (anion) to a solution containing cations of the appropriate metal. If the precipitating ligand is added directly by simply pouring one solution into another then there is little control of the chemistry during precipitation because of the large and inhomogeneous gradients in solution concentration. A better control of chemical and morphological characteristics can be achieved if the precipitating ligands are generated "in situ", simultaneously and uniformly throughout the solution, this results in what is known as a "homogeneous" precipitation process.

A homogeneous precipitation process based on forced hydrolysis is quite widely applicable and has been used to produce various monodisperse metal oxide precursor particles of various shapes and sizes [see MATIJEVIC, in High Tech Ceramics, edited by P.Vincenzini, (Elsevier, Amsterdam, 1987) p. 441-458]. Forced hydrolysis is usually accomplished either by increasing the pH of the solution, or by heating the solution, in some cases at temperatures up to boiling point at atmospheric pressure, but more usually to higher temperatures under pressure, i.e. hydrothermal treatment.

In the present specification, the term "hydrothermal treatment" of a substrate means heating said substrate in the presence of water at a temperature above the normal boiling point of the water under applied or autogenous pressure sufficient to prevent boiling of the water.

Homogeneous precipitation by an increase in the pH of the solution can be achieved by the thermal decomposition of urea or hexamethylenetetramine to form ammonia thereby generating OH^- as the precipitating ligand [see MATIJEVIC, in High Tech Ceramics, edited by P.Vincenzini, (Elsevier, Amsterdam, 1987) p. 441-458]. Monodispersity of the precipitated particle results from the occurrence of nucleation in a single burst followed by a uniform growth process, for example according to the LaMer theory. The primary particles resulting from such a nucleation process are usually monodisperse and several nanometers in size. Amorphous precipitates such as aluminium hydroxide usually consist of spherical particles whereas crystalline precipitates

often consist of faceted particles. Ageing of such a solution usually leads to agglomeration of the primary particles to form densely packed agglomerates. The agglomerates often have a fairly narrow size distribution and tend to be spherical in the case of amorphous precipitates where there is no ordering force such as a dipole moment or a difference in the surface energy between the crystal facets of the primary particles. Agglomerates as large as 1 micron in diameter can be obtained.

There are several reports of methods for the preparation of cerium oxide that depend on an increase in pH to cause precipitation. Matjevic and Hsu [see MATIJEVIC and W.P.HSU, *J. Colloidal Interface Sci.*, **118** (1987) 506-523] obtained non-spherical crystalline particles of $CeO(CO_3)_2H_2O$ by precipitation with urea. Aiken et al [see AIKEN, W.P. HSU and E.MATIJEVIC, *J. Am. Ceram. Soc.*, **71** (1988) 845-85] used the same method to obtain spherical particles of a mixed Y(III)/Ce(III) compound. Akinc and Sordelet [see AKINC and D.SORDELET, *Advanced Ceramic Materials*, **2** (1987) 232-238] prepared non-spherical well-crystallised $CeOHCO_3$ particles. Chen and Chen [see CHEN and I.W. CHEN, *J. Am. Ceram. Soc.*, **76** (1993) 1577-1583] used hexamethylenetetramine decomposition to prepare cerium oxide powders and compared them with those precipitated with ammonium hydroxide.

Heating the solution to force hydrolysis has been reported by several authors. Briois et al [see BRIOIS, C.E.WILLIAMS, H. DEXPERT, F.VILLAIN, B. CABANE, F. DENEUVE and C.MAGNIER, *J. Mat. Sci.*, **28** (1993) 5019-5031] reported the preparation of 3nm particles of $CeOSO_4H_2O$ from Ce(IV) sulphate at 90°C, but this is not

an attractive precursor for cerium oxide due to the presence of the sulphate group.

Hydrothermal conditions appear more suitable for the direct preparation of cerium oxide. Hirano and Kato [see HIRANO and E. KATO, *J. Am. Ceram. Soc.* **79** (1996) 777-780] obtained fine cerium oxide from Ce(III) nitrate, Ce(IV) sulphate and Ce(IV) ammonium sulphate solutions at 180°C under autogenous pressure. Stable suspensions of well crystallised cerium and cerium oxide doped with 6 at% Y were hydrothermally synthesised at temperatures up to 300°C by Yang and Rahman [see YANG and M.N. RAHAMAN, *J. Eur. Ceram. Soc.,* 17 (1997) 525-535].

The homogenous precipitation results cited above, which all depend on forced hydrolysis to cause precipitation succeed in controlling agglomerate morphology and yield agglomerates with a narrow size distribution. However, in the case of precipitation by increase of pH, the agglomerates are densely packed and because the primary particles tend to be strongly bound together by surface forces, the resulting agglomerates are not easily redispersed. Hydrothermal treatment is generally more successful in producing weakly-agglomerated and well-crystallised powders, but the crystallite size tends to be considerably larger. These results demonstrate that powder characteristics are sensitively dependent on the method of preparation so that, in principle, there is considerable scope to try to engineer the powder properties to suit a particular application. Uniformly-sized crystallites smaller than 5nm, or loosely-bound agglomerates have been produced with the methods mentioned above, but obtaining both characteristics in one powder with them

has been difficult to achieve. Forced hydrolysis by increase of pH or temperature is the common factor in these methods, and if it is this that restricts the range of powder properties that can be achieved, then alternative precipitation chemistries are required to provide better routes to weakly-agglomerated nanoscale powders.

It is an object of the present invention to address at least some of the problems associated with methods of homogeneous precipitation known in the art.

Accordingly, in a first embodiment, the present invention provides a process for inducing homogeneous precipitation of a metal oxide, wherein said metal is capable of existing in at least two cationic oxidation states, which process comprises the steps of,

(i) providing an aqueous solution of a metal in a lower cationic oxidation state and,

(ii) adding an oxidant capable of oxidising said metal to a higher cationic oxidation state under conditions such that the mixing of said aqueous solution and said oxidant is substantially complete before precipitation of an oxide of said metal in its higher oxidation state occurs.

The precipitation process of the present invention may include the further step of isolating the resultant precipitate by, for example, filtration, sedimentation, electrophoresis or centrifugation. The process may also further include the steps of washing and drying the isolated precipitate.

It is necessary for mixing to be substantially

complete before oxidation sufficient to result in precipitation of said metal oxide has occurred because this means that precipitation is delayed until a homogeneous mixture is formed. This ensures that homogeneous precipitation results.

Preferably, the metal oxide which precipitates out of solution is a product of hydrolysis of the metal in its higher cationic oxidation state. Metal ions in their higher cationic states have a greater charge density than those in their lower cationic oxidation state are therefore frequently more susceptible to hydrolysis in aqueous solution.

Metal hydroxides, hydrated metal oxides, metal oxohydroxides, and metal oxoperoxohydroxides (herein referred to collectively as "metal oxides")are commonly the products of metal cation hydrolysis.

It will be appreciated by a person skilled in the art that the metal may be selected from many metals which are capable of existing in at least two cationic oxidation states. Preferably, the metal is selected from Ce or Fe. Ce can exist in the +III and +IV oxidation states whilst Fe can exist in the +II and +III oxidation states.

The counter-ion to the metal in its lower oxidation state may be any inorganic anion which provides a soluble salt of the metal in its lower oxidation state. Preferably, the counter-ion is selected from one or more of nitrate, chloride, sulphate, phosphate, fluoride, bromide, and iodide. Most preferably the counter-ion is a nitrate ion because nitrate ions invariably confer high aqueous solubility on their

metal salts.

It will be appreciated by those skilled in the art that the concentration of the aqueous solution of said metal in a lower cationic oxidation state will depend on the identity of the metal ion and its counter-ion and possibly also on the identity of the oxidant used in the process. However, in a preferred embodiment the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/l, preferably 0.05 to 0.2. More preferably, the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/l.

It will also be appreciated by those skilled in the art that a number of suitable oxidants may be used to effect oxidation of the metal from its lower cationic oxidation state to its higher cationic oxidation state. Preferably, the oxidant is present as a solution in a water-miscible solvent, more preferably as an aqueous solution. In a particularly preferred embodiment, the oxidant comprises hydrogen peroxide. Hydrogen peroxide is particularly preferred because it does not contaminate the end product with additional anion species. More preferably, the oxidant comprises an aqueous solution of from 3% to 50% hydrogen peroxide in water. In a still more preferred embodiment the aqueous solution of an oxidant comprises approximately 30% hydrogen peroxide in water. Potassium permanganate is another possible oxidant. Preferably, potassium permanganate is added as an aqueous solution.

When hydrogen peroxide is used as the oxidant the

metal oxide which precipitates out of solution may have the general formula $M(OH)_{x-y}OOH_y$ wherein x is equal to the oxidation state of the metal cation M and $y \geq 1$. For example, when the metal in its lower oxidation state is Ce^{3+} and the metal in its higher oxidation state is Ce^{4+} the metal oxide which precipitates out of solution has the general formula $Ce(OH)_{4-y}OOH_y$ wherein $y \geq 1$.

It will be appreciated by those skilled in the art that a number of suitable methods may be used to reduce the rate oxidation of the metal from its lower cationic oxidation state to its higher cationic oxidation state. However, in a preferred embodiment the rate of oxidation is slowed by cooling the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant (hereinafter referred to as the reactants) prior to mixing. More preferably, both reactants are cooled to a temperature in the range of from -10°C to 10°C prior to mixing. Even more preferably, both reactants are cooled to a temperature in the range of 0 to 5°C prior to mixing.

The process of the present invention is distinguished from the prior art in that precipitation is induced by a change in oxidation state of the cation and not by an increase in pH or temperature.

Advantageously, the homogeneous precipitation process comprises the additional step of adding hydroxide ions to the mixture of the reactants so as to substantially complete the precipitation process. Preferably, said hydroxide ions are provided by the addition of aqueous ammonium hydroxide. Preferably the ammonium hydroxide has a concentration in the range of from 5 to 33 vol%,

more preferably approximately 25 vol%.

The homogeneous precipitation process of the present invention, including the step of adding hydroxide ions, provides metal oxides which are suitable precursors for the generation of weakly agglomerated nanocrystalline powders of said metal oxides. Accordingly, in a second embodiment, the present invention provides a process for the preparation of a weakly agglomerated nanocrystalline powder of a metal oxide, which process comprises the steps of,

i) inducing homogeneous precipitation of said metal oxide by a process as hereinbefore described in the first embodiment including the additional step of adding hydroxide ions to the mixture of the first and second solutions so as to substantially complete the precipitation process,

ii) isolating the precipitate.

Preferably, the process includes the further step of subjecting the isolated precipitate to hydrothermal treatment.

The process may also include the further steps of washing and drying the resultant precipitate.

Step ii) may be achieved, for example, by filtration, sedimentation, electrophoresis or by use of a centrifuge.

Preferably, said hydrothermal treatment comprises heating the precipitate in an autoclave in the presence of water at a temperature of from 100 to

300°C, more preferably, at a temperature of from 150 to 200°C, most preferably, at a temperature of approximately 180°C.

As stated above the pressure used for the hydrothermal treatment is that sufficient to prevent boiling of the water. This will obviously depend upon the temperature. At lower temperatures, i.e. up to 220°C, sufficient pressure may be generated by the vapour pressure of the water in the sealed vessel, i.e. from 5 to 50 bar. At higher temperatures, i.e. greater than 220°C, pressure may need to be applied, i.e. up to 150 bar.

The present invention also includes within its scope a metal oxide produced by the homogeneous precipitation process as hereinbefore described in the first embodiment.

The present invention also includes within its scope a weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as hereinbefore described in the second embodiment.

Preferably, the metal oxide or weakly agglomerated nanocrystalline powder of a metal oxide has a mean particle size in the range of from 2 from 10 nm with a geometric standard deviation, σ_g, less than or equal to 1.2. More preferably in the range of from 2 to 5 nm with a geometric standard deviation, σ_g, less than or equal to 1.1.

Particularly preferred metal oxides, and particularly preferred weakly agglomerated nanocrystalline powders of a metal oxide, are those which comprise cerium (IV)

oxide.

The present invention also includes within its scope a glass, a polishing medium for glass, a thin surface film, a phosphor, an oxygen storage material or a catalyst material which has been manufactured by a process which uses a weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as hereinbefore described in the second embodiment.

In a particularly preferred embodiment of the present invention, a nanocrystalline powder of cerium oxide is prepared from aqueous cerium (III) nitrate solution by a two-stage precipitation process which yields weakly-agglomerated powders with a crystallite size smaller than 5nm. In this embodiment a 30% aqueous solution of hydrogen peroxide is added to an aqueous solution of cerium nitrate at 5°C to slowly oxidise Ce^{3+} to Ce^{4+} and thereby initiate homogeneous precipitation of 3-4nm primary particles and the formation of dense spherical agglomerates. The precipitation process is completed by the addition of ammonium hydroxide which disrupts the spherical agglomerates leaving a weakly-agglomerated powder of hydrated cerium oxide. The process is completed by hydrothermal treatment at 180°C.

Precipitation is therefore induced by a change in oxidation state of the cation and not by an increase in pH or temperature. The product of the reaction is believed to be $Ce(OH)_3OOH$ and not $Ce(OH)_4$ which is otherwise obtained when ammonium hydroxide alone is used as the precipitating agent.

The present invention will be further illustrated with reference to the following examples and comparative examples

The starting materials used in the following examples were: cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$, anal., Alfa-Johnson Matthey), hydrogen peroxide (30% H_2O_2, p.a., Merck) and ammonium hydroxide (NH_4OH, 25 vol% p.a., Merck).

Three synthesis routes, referred to as methods A, B and C, were used for preparation of cerium oxide powder as described below.

Method A (Comparative Examples A1 and A2)
Ammonium hydroxide was added dropwise to a stirred solution of 0.1 mol/l Ce(III) nitrate in water until a solution pH of 10 was reached. A white or yellowish gel-like precipitate was formed which settled rapidly. A sample of the gel-like initial precipitate was prepared for analysis by taking a portion of the reaction mixture, decanting the solution and washing the precipitate twice with a double volume of distilled water and then drying at 80-85°C overnight (Example A1). The remainder of the product, i.e. supernatant + precipitate, was hydrothermally treated at 180°C for 4 hours under autogenous pressure without stirring to obtain cerium oxide. After cooling, the clear solution was decanted and the yellowish precipitate was washed with about 200ml distilled water and then dried at 80-85°C overnight (Example A2).

Method B (Examples B2 and B3 are Comparative)
A solution of 0.1 mol/l Ce(III) nitrate in water was

mixed with 30 vol% hydrogen peroxide in a volume ratio of 3 parts Ce(III) nitrate to 1 part hydrogen peroxide at various temperatures: at about 5°C (Example B1), at room temperature (Example B2), and a solution which was mixed at RT and then heated to boiling temperature (Example B3). An orange-yellow transparent sol appeared in all cases: after 8-10 minutes at 5°C and after 2-3 minutes at RT, or on heating to boiling point. The sol produced at 5°C and aged at that temperature for 12h was stable at room temperature for more than one week without any settling of the solid phase. In contrast, solids produced at room temperature and by heating to boiling partially sedimented. The precipitated solid particles (Examples B1, B2 and B3) were separated by centrifugation for further examination.

Method C

Separate solutions of 0.1 mol/l Ce(III) nitrate in water and of 30 vol% hydrogen peroxide were cooled to 5°C and then mixed together under constant stirring. After 8-10 minutes the solution turned first yellow then orange-yellow, but remained transparent, and a sol was formed. Ammonium hydroxide solution was then added to increase the pH value to 10. Above a pH of 9-9.2 the pH increased only slowly in response to further addition of ammonium hydroxide solution and an orange precipitate settled rapidly from solution. Precipitation therefore occurred in two stages. The solution was decanted and the precipitate was washed and dried at 80-85°C (example C1) or hydrothermally treated (example C2) as described under method A (example A2) above.

Samples of the powders synthesised by methods A, B and

C were calcined in air to 300°C and 500°C in alumina crucibles at a heating rate 2°C/min with a dwell time of 1h at temperature.

The precipitated cerium oxide precursors and calcined products were characterised using several techniques known to those skilled in the art to determine particle size, composition and morphology.

Differential thermal analysis and thermogravimetric analysis (DTA/TG, Netsch STA 409) were conducted in a dry-air atmosphere using a heating rate of 2°C/min.

Samples for transmission electron microscopy (TEM, Philips EM 400) of the precipitated cerium oxide precursors were prepared by dipping carbon-coated copper grids into a dilute water suspension of the particles immediately after synthesis. The grids were then dried at room temperature or at 80-85°C. The calcined product was dispersed in absolute ethyl alcohol by ultrasonification (3-5 min) and a drop of a suspension was allowed to evaporate on the grid at room temperature. X-ray diffraction analysis (XRD, Philips PW173) was used to determine phase composition and to estimate the crystallite size of the powders. A 2θ range of 5-80° was used and the apparent crystallite size was estimated from peak broadening using the Scherrer equation: $D_{app} = K \lambda / (B \cos\theta)$, where K = 0.9 and B = peak width obtained using a Voigt peak fitting routine. CuK_α radiation with a graphite filter was used ($\lambda = 1.5406$) and the instrumental broadening was determined using a LaB_6 standard.

The precipitates produced by the 3 different methods

differed significantly, primarily due to the presence of different anion species (-OH in method A, -OOH in method B, or -OH + -OOH in method C) and to the reaction temperature used.

The use of ammonium hydroxide alone (method A) resulted in voluminous white or yellowish gel-like precipitate from Ce(III) nitrate solution. In principle the precipitate should be $Ce(OH)_3$, which is white and is a definite compound rather than a hydrous oxide. Oxidation of Ce^{3+} to Ce^{4+} in solution has been suggested at high pH, i.e. $Ce^{3+} + H_2O \rightarrow Ce(OH)^{3+} + H^+ + e^-$ with subsequent hydrolysis to $Ce(OH)_4$ and precipitation. However, oxidation of $Ce(OH)_3$ also occurs readily in air at room temperature to form yellow $Ce(OH)_4$. $Ce(OH)_4$ is a hydrous oxide which can also be described as $CeO_2.2H_2O$ which dehydrates progressively i.e. $CeO_2.nH_2O$ where $n \leq 2$. The product of precipitation with ammonium hydroxide is therefore likely to be $CeO_2.nH_2O$ rather than $Ce(OH)_3$.

Precipitation from Ce(III) nitrate using hydrogen peroxide alone (method B) resulted in a fine solid which formed faster at boiling temperature (example B3) than at 5°C (example B1) or at room temperature (example B2). The stability of the solid solution, as defined by the first appearance of settled solid, was more than 1 week for solid produced at 5°C, and a few minutes for solid produced at boiling temperature. Hydrogen peroxide alone was not capable of precipitating all cerium ions from solution Complete precipitation of cerium ions was achieved using hydrogen peroxide + ammonium hydroxide (method C). The orange-yellow precipitate was formed by a two step process, first the initiation of hydrolysis and

complexation with hydrogen peroxide followed by quantitative precipitation with ammonium hydroxide to a pH of about 10. The precipitate settled rapidly and it was easily separated from solution. The precipitates were stable in water but the dry precipitate slowly transformed to crystalline cerium oxide in air at room temperature.

Cerium oxide was identified in the X-ray diffraction spectra of all the powders. The peaks in the spectra of powders precipitated by ammonia alone (method A) were narrow and well-defined with a high signal-to-noise ratio; those of the other powders were all much broader and less intense. Peak broadening may be attributed to small crystallite size and apparent crystallite sizes were calculated as shown in table 1. The cerium oxide powder derived from the -OH (method A) and -OOH + -OH (method C) precipitates by hydrothermal treatment (examples A2 and C2) were both weakly agglomerated, but the powder from mixed ligand precipitation had a significantly smaller apparent crystallite size (4.2nm compared with 26.8nm).

Information about the chemical composition of the precipitates was deduced from the thermogravimetric weight loss measurements by comparing measured values with the theoretical weight losses for plausible decomposition reactions e.g. the decomposition of hydrated oxide i.e., $CeO_2.2H_2O$ to CeO_2 should result in a weight loss of 17.29%. The XRD spectra indicated that CeO_2 was present in all samples, but the additional presence of amorphous $Ce(OH)_4/CeO_2.nH_2O$ could not be excluded.

The precipitate obtained by method A (addition of

ammonium hydroxide alone) after drying overnight at 80-85°C (example A1) showed a weight loss of 6.2% and a weight loss of 3.1% after hydrothermal treatment (example A2), as shown in Figures 1A and 1B. These weight losses are lower than those corresponding to the decomposition of $Ce(OH)_3$ (9.95%) or $Ce(OH)_4/CeO_2.2H_2O$ (17.3%) and indicate that the samples consisted either of a partially hydrated form of cerium oxide, i.e. $CeO_2.nH_2O$, for which a 6.2% weight loss on decomposition corresponds to n = 0.59, or that it consisted of a mixture of phases e.g. CeO_2 + $CeO_2.2H_2O$. A weak exothermic peak at about 280°C, which might correspond to the crystallisation of anhydrous cerium oxide, was clearly present in Figure 1A, but was scarcely evident in Figure 1B for the hydrothermally treated sample.

The precipitate obtained by method B (precipitation with hydrogen peroxide alone) showed a total weight loss of 16.8% for the precipitation procedure carried out at boiling point as shown in figure 2. This total weight loss corresponds well with that expected for $Ce(OH)_4/CeO_2.2H_2O$ decomposition (17.3%). The general shape of the weight loss curve was similar to that in Figures 1A and 1B, i.e. the decomposition appeared to occur in 3 distinct stages and was not complete until >800°C, but the DTA curve did not show the exothermic peak at 280°C that was observed in Fig 1A.

The precipitate obtained by method C (precipitation with hydrogen peroxide followed by ammonium hydroxide) at 5°C showed a total weight loss of 23.0% as shown in Fig 3 which corresponds closely to that expected for the decomposition of $Ce(OH)_3OOH$ (23.2%) assuming that a single phase was initially present. The DTA curve in

Fig 3A showed two well-defined events. The first event produced an endothermic peak at about 80°C, which might be due to dehydration, or it might correspond to the transformation; $Ce(OH)_3OOH \rightarrow Ce(OH)_4/CeO_2.2H_2O$, with a theoretical weight loss of 7.1%. The second event generated a well-defined exothermic peak at 250-280°C which might correspond to the crystallisation of CeO_2 occurring at a slightly lower temperature than in the case of that obtained with method A (see Fig 1A). After ageing freshly-prepared precipitate for 4h at 100°C the TG weight loss was 15.1% which does not correspond to the decomposition of any single compound and would be consistent with the presence of a mixture of species due to the complete decomposition of the initial phase e.g. of $Ce(OH)_3OOH$ to $Ce(OH)_4/CeO_2.2H_2O$ and the partial decomposition of $CeO_2.2H_2O$ to $CeO_2.nH_2O$ where n<2. The DTA curve was consistent with the interpretation of the TG curve given above i.e. it no longer showed an endothermic peak at 80°C and the exothermic peak at 250-280° was still present but was slightly less intense compared with that for the precipitate prepared at 5°C.

TEM analysis provided information on the size and shape of primary particles and their state of agglomeration. The general morphology of the particles precipitated by ammonium hydroxide (method A) is shown in Fig 4A. The precipitate consisted of non-uniform agglomerates of equiaxed crystallites approximately 3-4nm diameter. On calcination there was considerable grain coarsening and the agglomerates were hard and non-dispersable Fig 4B. Hydrothermal treatment of the hydroxide precipitate resulted in non-agglomerated uniform cubic crystallites 15-20 nm in diameter as shown in Fig 4C. The hydrothermally treated powder

exhibited considerable coarsening of crystallite size after calcination for 1h at 300°C, Fig 4D.

Particles obtained by precipitation with hydrogen peroxide (method B) at room temperature (example B2) consisted of dense agglomerate of crystallites 3-4nm in diameter as shown in Figures 5A and 5B. Crystallisation of cerium oxide could be observed under the electron beam during TEM examination. Figures 5C and 5D shows particles produced by precipitation with hydrogen peroxide at 5°C (example B1). The crystallites were slightly smaller at 2-3nm than in the sample precipitated at room temperature. Figures 5E and 5F show particles precipitated by hydrogen peroxide at 85°C (example B3). The densely-packed equiaxed agglomerates of 50-100 nm diameter that were obtained are typical of agglomerates formed during homogeneous precipitation and consisted of randomly oriented primary crystallites of 3-4nm i.e. similar in size to those precipitated at RT. Crystallite size coarsened considerable on calcination. Sharply-facetted crystallites as large as the agglomerates were observed after 1h at 300°C - Fig 5G.

Particles from the two-stage precipitation at 5°C with hydrogen peroxide and ammonium hydroxide (method C) are shown in Figures 6A and 6B for powder dried at 120°C for 2h. The agglomerate structure was much less densely packed than in the samples precipitated with H_2O_2 alone and consisted of randomly-oriented uniform crystallites 5-8nm in diameter. The powder obtained from this sample after hydrothermal treatment (example C2)is shown in Figures 6C and 6D. The crystallites were uniform and about 5nm in diameter and appeared to

be loosely agglomerated. After calcination for 1h at 500°C there was very little change in crystallite size.

The reference product was powder produced by method A i.e. the precipitation of cerium hydroxide from Ce(III) nitrate by the addition of ammonium hydroxide. The XRD spectra of the precipitate dried at 80°C (example A1) showed that the product consisted of well-crystallised CeO_2 and TG weight loss measurement indicated it to be slightly hydrated, so that a transformation must have occurred on drying the powder e.g.:

$$Ce(OH)_4 \rightarrow CeO_2.2H_2O \rightarrow CeO_2.nH_2O$$

This method yielded agglomerates with a wide size distribution and which were hard and non-dispersible after calcination and therefore not suitable for further processing. However, hydrothermal treatment of the wet precipitate (example A2) yielded weakly-agglomerated cubic crystallites that were suitable for further processing. The crystallite size was 15-20nm in size according to TEM images and about 27nm according to XRD peak broadening. The hydrothermal treatment therefore solved the problem of hard agglomerates with this material, but at the expense of considerable crystal growth. In contrast, method C yielded a weakly-agglomerated powder which was not subject to crystal growth during hydrothermal treatment and which had a crystallite size of about 5nm according to XRD measurement and which appeared somewhat smaller in TEM images, although the image magnification was too low for an accurate measurement.

A key feature of the method C was to mix together hydrogen peroxide and cerium (III) nitrate solution as a temperature low enough to prevent immediate reaction e.g. about 5°C. Maintaining the solution at a constant low temperature ensured that subsequent precipitation occurred homogeneously and that a stable sol formed.

The composition of the dried sol particles precipitated with H_2O_2 alone (method B) as deduced from TG was $Ce(OH)_4/CeO_2.2H_2O$ (measured weight loss = 16.8%, theoretical weight loss = 17.3%). Precipitation of a hydroxide in an acidic solution seems unlikely, but it could form during the drying procedure due to the limited stability of lanthanide peroxides. The crystallite size of about 3nm is also an indication that the precipitation mechanism differed form that with ammonium hydroxide which yielded crystallites about 5 times layer. The role of the peroxo ligand during precipitation may have been to reduce the crystallite growth rate by changing the surface properties or morphology of the particles.

Addition of ammonium hydroxide to the sol (method C) resulted in further precipitation of cations from solution to yield an orange precipitate for which a composition of $Ce(OH)_3OOH$ was deduced from TG (measured weight loss = 23%, theoretical weight loss = 23.2%). This was the composition deduced for the dried product but, given the uncertainty about the stability of the lanthanide peroxides, it may be more appropriate to describe the precipitate that formed in solution by the general formula $Ce(OH)_{4-x}OOH_x$ with $x \geq 1$ for the precipitate formed at 5°C. The x=1 composition appeared to be stable enough to withstand drying at 80°C but did not withstand 4h at 100°C. The use of

ammonium hydroxide in the second stage of method C not only completed the precipitation process of method B but also disrupted the dense agglomerates formed by H_2O_2 precipitation as can be seen by comparing Fig 5 and Fig 6. Loosely-agglomerated powder should be less subject to crystallite growth on calcination in proportion to the reduced number of contact points between crystallites. Crystallite growth was insignificant during hydrothermal treatment of samples precipitated with hydrogen peroxide and ammonium hydroxide, and the crystallite size remained under 5nm. In samples precipitated with ammonium hydroxide alone, crystallite size almost doubled to over 25nm under the same conditions. It is difficult to attribute the suppression of crystallite growth during hydrothermal treatment to the continued presence of the peroxo group, which is believed to be unstable at the temperatures used i.e. 180°C. The addition of ammonium hydroxide in method C therefore appears to be an important factor in the prevention of hard agglomerates which might otherwise transform to single crystals on heating as shown in Fig 5G. Crystallites smaller than 5nm were reported previously only in the case of precipitation of $CeOSO_4.H_2O$ from Ce(IV) sulphate solution. In contrast to the nitrate group, the sulphate group is not easily decomposed on calcination, and sulphate is therefore generally not acceptable in a cerium oxide precursor.

The method of inducing homogeneous precipitation by the oxidation of the cation to a higher valence state with an increased hydrolysability, in this case Ce(III)/Ce(IV), is also applicable to other materials e.g. Fe(II)/Fe(III). An advantage of using of hydrogen peroxide as an oxidising, complexing and precipitating

ligand is that it does not contaminate the end product with additional anion species.

The weakly-agglomerated state of the cerium oxide powder, the uniform crystallite size of under 5nm, and the absence of deleterious anion impurities are characteristics which make the powder suitable for a variety of ceramic forming processes and applications.

Powders precipitated by the new two-stage method are significantly more weakly agglomerated as well as having a smaller crystallite size i.e. less than 5nm.

Table 1:

Crystallite size of cerium oxide powders calculated from XRD peak broadening (Scherrer equation)

Sample preparation parameters			Crystallite size (nm) after thermal treatment		
Example	Temp	Autoclaved	12h at 80 - 85°C	1h at 300°C	1h at 500°C
A1	RT	no	15.4	15	27
A2	RT	yes	26.8	27	26
B3	100° C	no	3.2	4.4	-
C1	5°C	no	3.4	5.2	13
C2	5°C	yes	4.2	4.5	10

ART 34 AMDT

Claims:

1. A process for inducing homogeneous precipitation of a metal oxide, wherein said metal is capable of existing in at least two cationic oxidation states, which process comprises the steps of:

(i) providing an aqueous solution of a metal in a lower cationic oxidation state, and

(ii) adding an oxidant capable of oxidizing said metal to a higher cationic oxidation state under conditions such that the mixing of said aqueous solution and said oxidant is substantially complete before precipitation of an oxide of said metal in its higher oxidation state occurs,

wherein the rate of oxidation is reduced by cooling the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant prior to mixing.

2. A process as claimed in claim 1, wherein the aqueous solution of said metal in a lower cationic oxidation state and the oxidant are cooled to a temperature in the range of from -10 to 10°C prior to mixing.

3. A process as claimed in claim 2, wherein the aqueous solution of said metal in a lower cationic oxidation state and the oxidant are cooled to a temperature in the range of from 0 to 5°C prior to mixing.

4. A process as claimed in any one of the preceding claims, wherein the metal oxide which precipitates out of solution is a product of hydrolysis of the metal in

its higher cationic oxidation state.

5. A process as claimed in any one of the preceding claims, wherein the oxidant is added as an aqueous solution.

6. A process as claimed in any one of the preceding claims, wherein the metal is selected from Ce or Fe.

7. A process as claimed in any one of the preceding claims, wherein the aqueous solution of said metal in a lower cationic oxidation state comprises nitrate as a counter-ion.

8. A process as claimed in any one of the preceding claims, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/1.

9. A process as claimed in any one of the preceding claims, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/1.

10. A process as claimed in any one of the preceding claims, wherein the oxidant comprises hydrogen peroxide.

11. A process as claimed in claim 10, wherein the metal salt or oxide has the general formula $M(OH)_{x-y}OOH_y$ wherein X is equal to the oxidation state of the metal cation M and $y \geq 1$.

12. A process as claimed in claim 10 or claim 11, wherein the metal in its lower oxidation state is Ce^{3+}, the metal in its higher oxidation state is Ce^{4+} and the metal oxide which precipitates has the general

formula $Ce(OH)_{4-y}OOH_y$ wherein $y \geq 1$.

13. A process as claimed in any one of the preceding claims, comprising the additional step of adding hydroxide ions to the reaction mixture so as to substantially complete the precipitation process.

14. A process as claimed in claim 13, wherein said hydroxide ions are provided by the addition of ammonium hydroxide.

15. A process as claimed in any one of the preceding claims, comprising the further step of isolating the precipitate.

16. A process as claimed in claim 15, comprising the further step of washing and drying the isolated precipitate.

17. A process for the precipitation of a weakly agglomerated nanocrystalline powder of a metal oxide, which process comprises the steps of:

(i) inducing homogeneous precipitation of said metal oxide by a process according to claim 13 or claim 14; and

(ii) isolating the precipitate.

18. A process as claimed in claim 17, which further comprises the step of subjecting the precipitate to hydrothermal treatment.

19. A process as claimed in claim 17 or claim 18 comprising the further step of washing and drying the precipitate.

20. A process as claimed in any one of claims 17 to 19, wherein said hydrothermal treatment is at a temperature of from 100 to 300°C.

21. A process as claimed in any one of claims 17 to 20, wherein said hydrothermal treatment is at a temperature of approximately 180°C.

22. A metal oxide obtained by a process as claimed in any one of claims 1 to 16.

23. A weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as claimed in any one of claims 17 to 21.

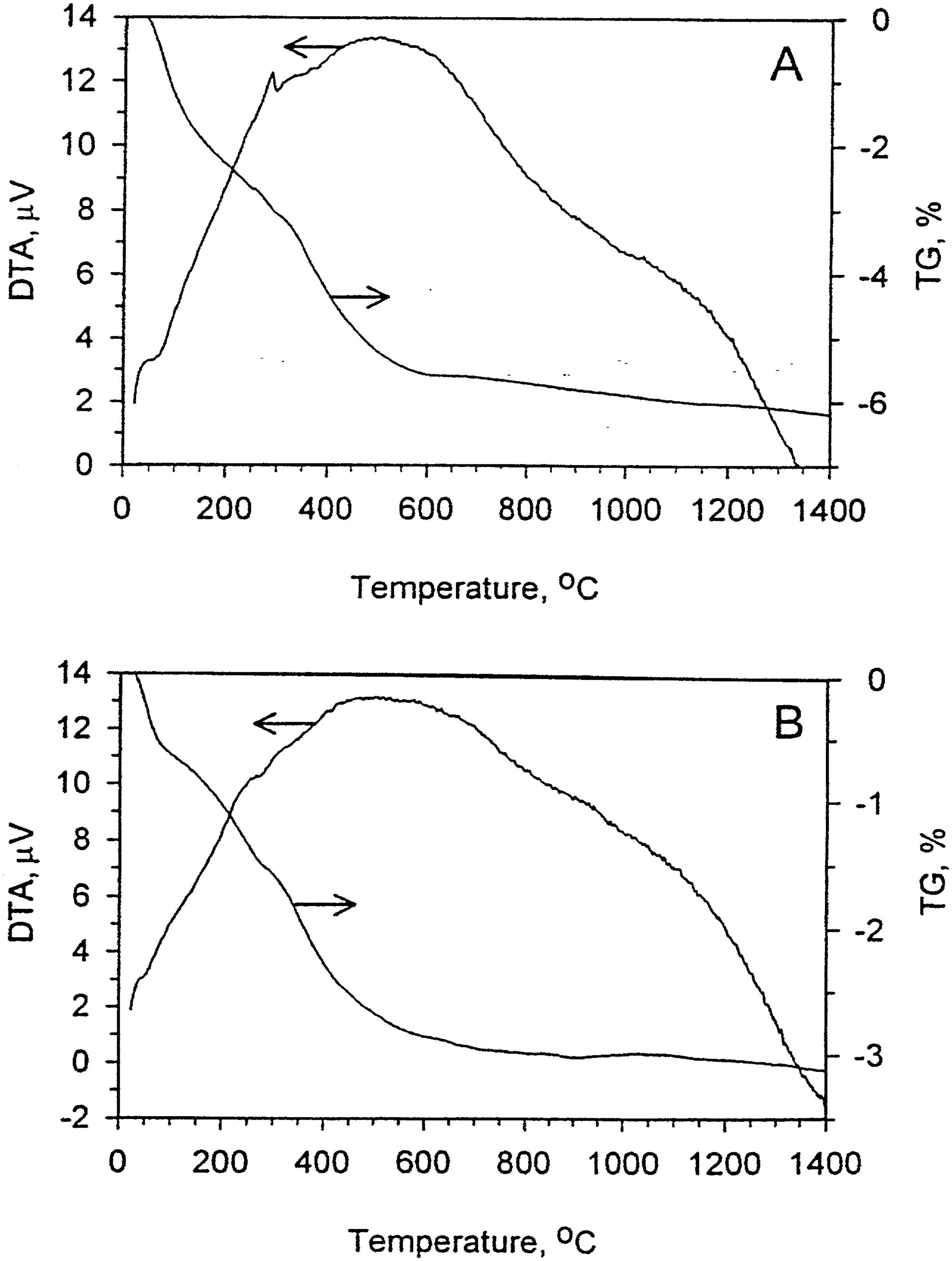
24. A metal oxide as claimed in claim 22 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 23 having a mean particle size in the range of from 2 to 10 nm with a geometric standard deviation in the particle size less than or equal to 1.2.

25. A metal oxide as claimed in claim 22 or claim 24 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 23 or claim 24 having a mean particle size in the range of from 2 to 5 nm with a geometric standard deviation in the particle size less than or equal to 1.1.

26. A metal oxide as claimed in any one of claims 22, 24 or 26 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in any one of claims 23, 24 or 25 which comprises cerium oxide.

27. A glass, a polishing medium for glass, a thin surface film, a phosphor, an oxygen storage material or catalyst material which has been manufactured by a

process which uses a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in any one of claims 23, 24, 25 or 26.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TG, %
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10
8
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Temperature, °C
B
DTA, µV
TG, %
14
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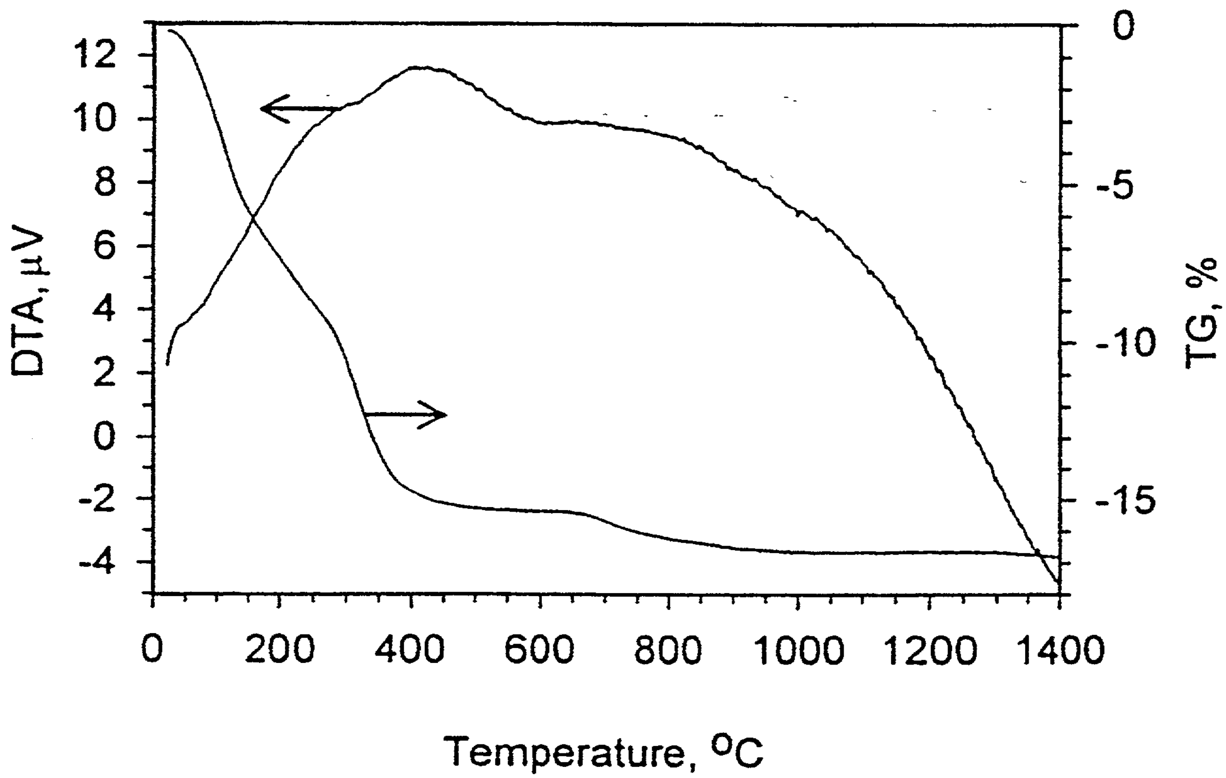
Temperature, °C

FIG. 1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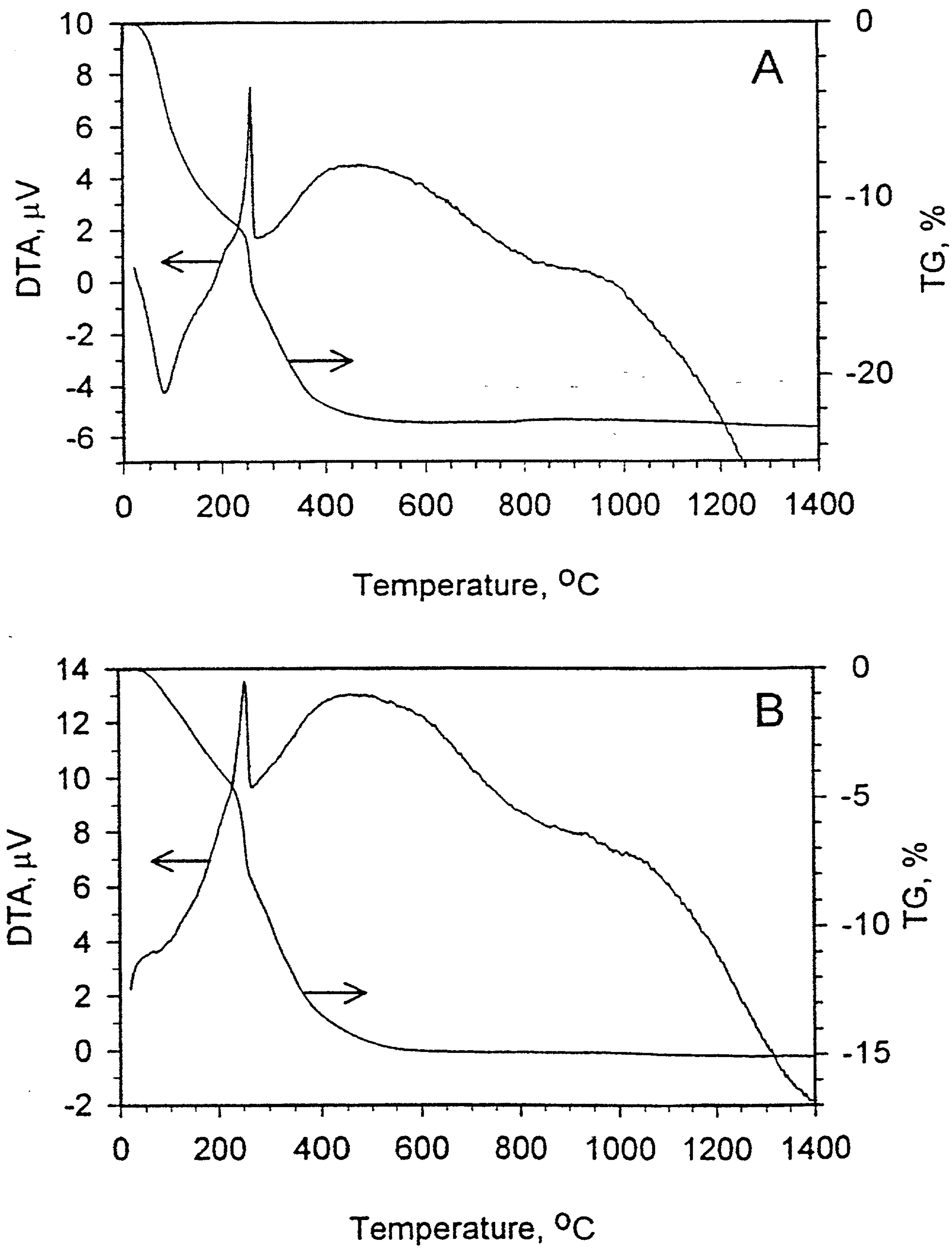
Temperature, °C

FIG. 2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Temperature, °C
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DTA, μV
TG, %
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6
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1400
Temperature, °C

FIG. 3

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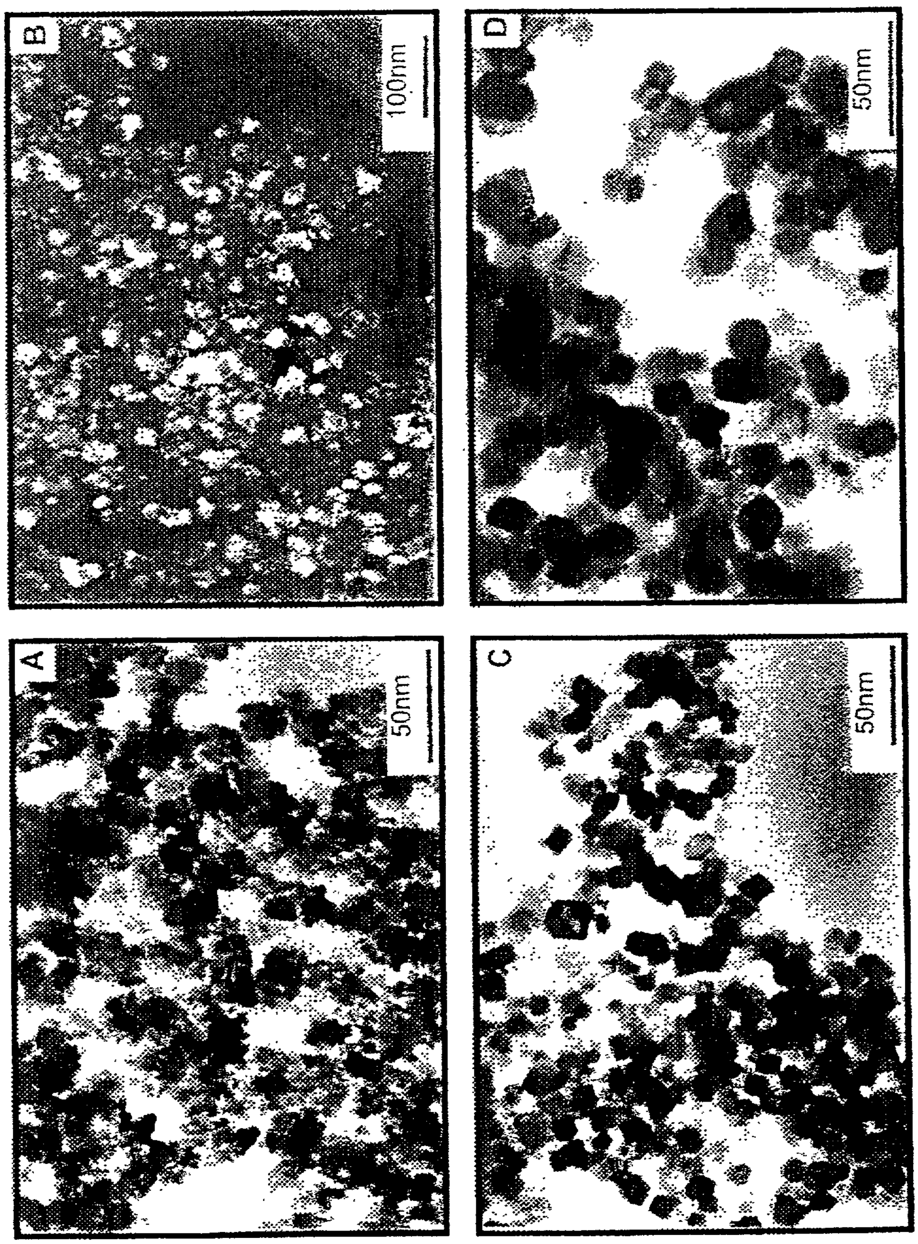

FIG. 4

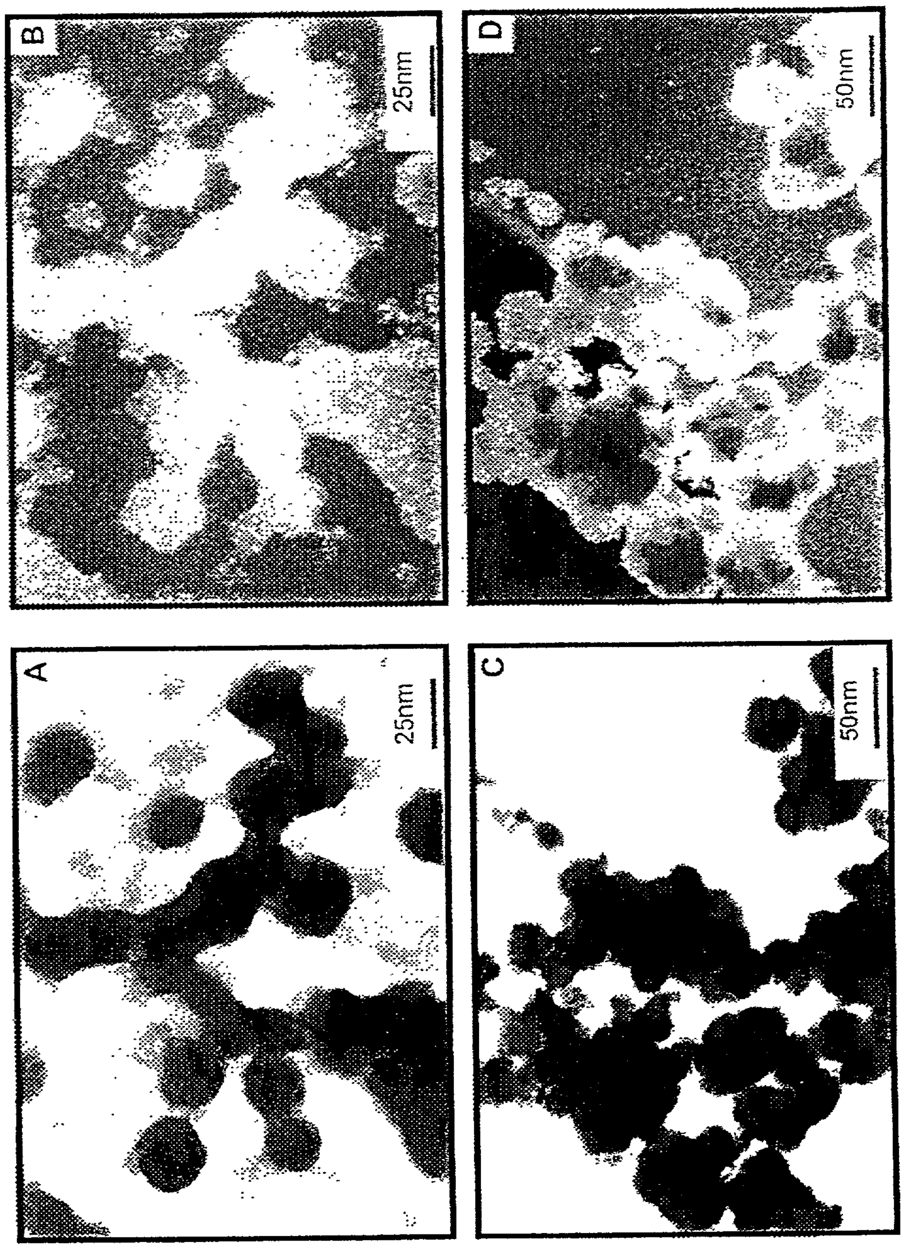

FIG. 5

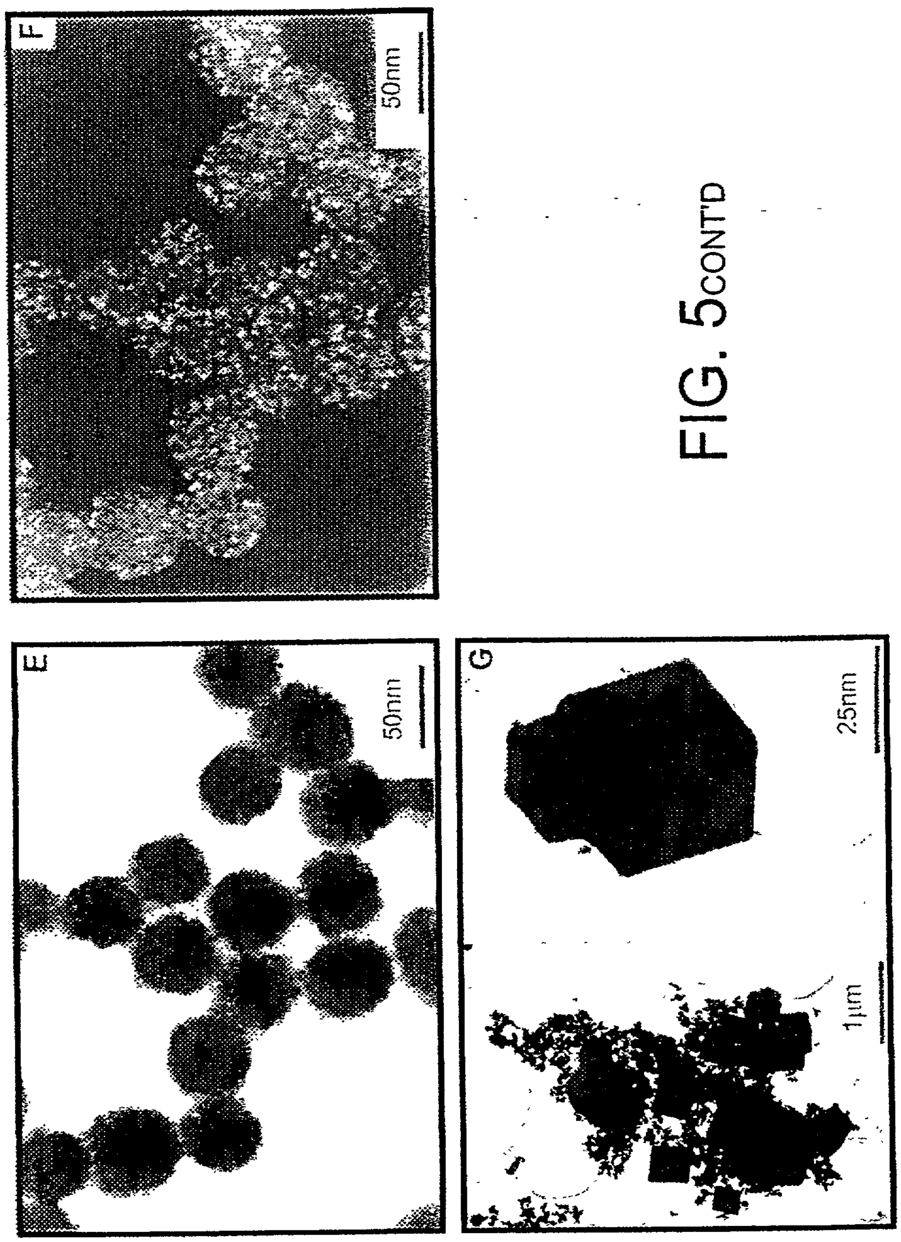

FIG. 5CONT'D

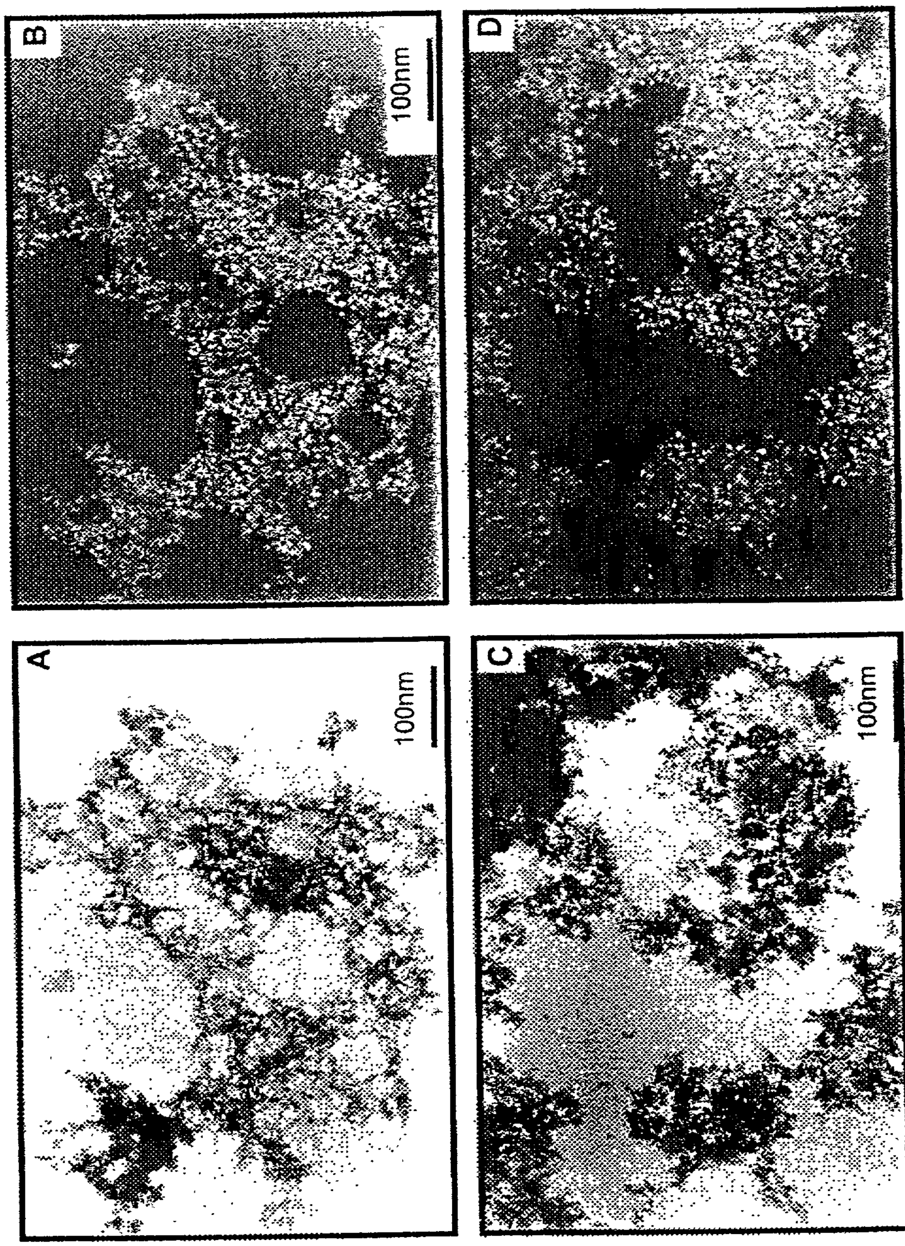

FIG. 6

#3

ATTORNEY/DOCKET NO:

DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention (Design, if applicable) entitled:

PRECIPITATION PROCESS

the specification of which (check one):

☐ is attached hereto, or ☒ was filed on: 15 February 2000 as U.S. Application Number or PCT International Application Number: PCT/GB00/00513
and (if applicable) was amended on:

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, §1.56*. I hereby claim foreign priority benefits under *Title 35, United States Code §119* of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)			PRIORITY CLAIMED	
Number	Country	Day/Month/Year Filed	Yes	No
9903519.8	United Kingdom (GB)	16/2/1999	X	

☐ Additional Priority Application(s) Listed on Following Page(s)

I HEREBY CLAIM THE BENEFIT UNDER TITLE 35 U.S. CODE §119(E) OF ANY U.S. PROVISIONAL APPLICATIONS LISTED BELOW.	
Application Number	Day/Month/Year Filed

☐ Additional Provisional Application(s) Listed on Following Page(s)

I hereby claim the benefit under *Title 35, United States Code, §120* of any United States application(s) or PCT international application(s) designating The United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of *Title 35, United States Code, §112*, I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, §1.56* which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Application Number	Filing Date	Status - Patented, Pending or Abandoned

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true: and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under *section 1001 of title 18 of the United States Code* and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

8

POWER OF ATTORNEY: I (We) hereby appoint as my (our) attorneys, with full powers of substitution and revocation, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: J. Ernest Kenney, Reg. No. 19,179; Eugene Mar, Reg. No. 25,893; Richard E. Fichter, Reg. No. 26,382; Charles R. Wolfe, Jr., Reg. No. 28,680; Thomas J. Moore, Reg. No. 28,974; Bruce H. Troxell, Reg. No. 26,592; Joseph DeBenedictis, Reg. No. 28,502; Benjamin E. Urcia, Reg. No. 33,805; and

I(we) authorize my(our) attorneys to accept and follow instructions from ______________________ regarding any matter related to the preparation, examination, grant and maintenance of this application, any continuation, continuation-in-part or divisional based thereon, and any patent resulting therefrom, until I(we) or my(our) assigns withdraw this authorization in writing.

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☒ *See following page(s) for additional joint inventors.*

ATTORNEY/DOCKET NO:

CONTINUATION OF DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

Page 2

PRIOR FOREIGN APPLICATION(S) (35 USC §119)			PRIORITY CLAIMED	
Number	Country	Day/Month/Year Filed	Yes	No

PRIOR PROVISIONAL APPLICATIONS 35 U.S. CODE §119(E)	
Application Number	Day/Month/Year Filed

PRIOR U.S. OR PCT INTERNATIONAL APPLICATIONS (35 U.S. CODE §120)		
Application Number	Filing Date	Status - Patented, Pending or Abandoned

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☐ *See following pages for additional joint inventors/priority applications.*